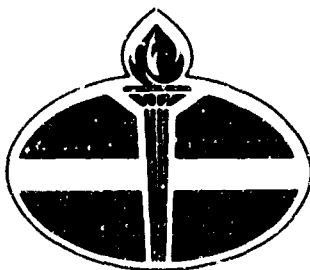


FINAL REPORT



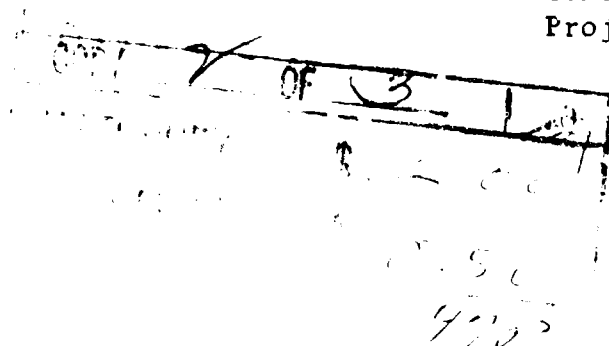
AMERICAN OIL COMPANY

RESEARCH AND DEVELOPMENT
DEPARTMENT

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Contract Nots-90267

Project Serial No. SR001-03-01, Task 606



DEVELOPMENT OF NONFLAMMABLE
HYDRAULIC FLUID

BUREAU OF SHIPS
Department of the Navy
Washington, D.C.

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Final Report

April 1, 1964 to June 1, 1965

DEVELOPMENT OF NONFLAMMABLE
HYDRAULIC FLUID

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FOREWORD

This report was prepared by the Research and Development Department of the American Oil Company under U.S. Navy, Bureau of Ships Contract Nobs-90267, Project Serial No. SR001-03-01, Task 606. Covered is work done from April 1, 1964 to June 1, 1965. The work was administered under the direction of the Chief Bureau of Ships, Code 634A, with Mr. E. C. Davis as technical monitor.

ABSTRACT

The object of this study was the development of a water-base hydraulic fluid which (1) yields a fire-resistant non-aqueous residue, (2) is compatible with materials of construction and sea-water contamination, (3) satisfactorily lubricates shipboard pumps, (4) presents no unusual storage or handling problems, and (5) exhibits no toxicological hazards under conditions of use.

Low-density polyethylene can be chlorophosphonated by reaction with phosphorus trichloride and oxygen. Hydrolysis and neutralization with potassium hydroxide yields products which satisfactorily thicken water and which have satisfactory fire-resistant properties. Potassium salts of low-molecular-weight phosphonic acids are satisfactory pour depressors for these fluids. Potassium chromate and potassium molybdate are effective corrosion inhibitors.

The most promising formula is:

27% Thickener
30% Potassium bis-Hydroxymethylphosphonate
2% Potassium Molybdate
41% Water

Properties of a typical sample of this fluid are:

Flash Point (°F)	640+
Fire Point (°F)	640+
Autogenous Ignition Temperature (°F)	1450+
Viscosity (cs. at 150°F)	30.2
Viscosity (cs. at 25°F)	659
Pour Point (°F)	-50
Specific Gravity (gm./ml.)	1.4

The fluid appears to be compatible with materials of construction and sea water, and to exhibit satisfactory storage-stability, shear-stability, filterability, and foaming characteristics. Fluid residues are removable by flushing with water. Screening tests in the Vickers Vane pump indicate that some improvement in antiwear properties may be necessary before satisfactory lubrication of shipboard pumps and bearings can be achieved.

Toxicity studies have shown the thickener-water blend to be substantially nontoxic. Toxicity studies on the finished fluid are being conducted. Results will be issued as an addendum to this report.

DEVELOPMENT OF NONFLAMMABLE HYDRAULIC FLUID

INTRODUCTION

Two types of fire-resistant hydraulic fluids are being used in aircraft-carrier systems. The fluid used in hydraulic catapults is a mixture of water, glycol, polyglycols, and additives. An aromatic phosphate ester fluid is used in aircraft elevators. Because of the complexity of submarine hydraulic systems, both of these fluids have serious shortcomings. The water-glycol fluids are incompatible with sea water, are relatively poor lubricants for heavily loaded bearings, and are corrosive to aluminum. In addition, loss of water results in the formation of flammable residues. Because of fluid-leakage problems, phosphate esters cannot be used in submarines.

A satisfactory water-base fluid for shipboard hydraulic-system use is needed. For the uses envisioned, fire resistance in both the finished fluid and the non-aqueous residue is of prime importance. In addition, the fluid must be capable of lubricating shipboard hydraulic pumps, be compatible with materials of construction and with 10% sea-water contamination, and present no unusual handling and storage problems. The fluid should be formulated to minimize toxicity hazards under conditions involving long periods of continuous exposure. Fluid residues should be removable by flushing with water.

In this study, the general approach consisted of the synthesis and evaluation of water-soluble thickening agents which exhibit satisfactory fire-resistant properties. Studies aimed at the development of additives to suppress metal corrosion and to lower pour point were conducted. Any toxicological hazards which may result from use of the fluid are being determined.

EXPERIMENTAL

At the beginning of this project, it was decided that a logical sequence for the development of a fluid having the desired properties would be to:

1. Develop a fire-resistant thickener.
2. Determine toxicity of the thickener.
3. Study the compatibility of fluids with materials of construction and with sea water.
4. Develop a suitable pour depressor.
5. Study the viscosity and shear-stability properties of fluids.
6. Obtain some information on the ability of fluids to lubricate.
7. Determine toxicity of final formulation.

Although considerable overlapping occurred during the study, this sequence was generally followed.

Development of Fire-Resistant Thickener

Two paths were followed in studies designed to develop appropriate thickeners: (1) chlorophosphonation of polyethylene followed by hydrolysis and neutralization of the product and (2) preparation and polymerization of esters of unsaturated organic acids of phosphorus.

Chlorophosphonation of Polyethylene

Numerous chlorophosphonations of polyethylene and similar materials were carried out to develop a procedure whereby a suitable thickener could be produced in laboratory equipment. The procedure described by Schroeder and Sopchak [J. Polymer Science 47, 417 (1960)] was followed with slight modifications. Table I summarizes the chlorophosphonations which led to the development of the procedure used to produce larger amounts of thickener for evaluation studies. From these studies, it can be concluded that:

1. Low-density polyethylenes having molecular weights of 1,200 to 21,000 react readily with PCl_3 and oxygen to form products from which thickeners can be prepared.
2. Use of too little PCl_3 results in unsatisfactory products. The optimum weight ratio of PCl_3 to polymer is 10-20 to 1.
3. FRS rubber, paraffin wax, mineral seal oil, and polybutene did not yield satisfactory products.

In all fluids studies, the polymer used was Union Carbide polyethylene DYL T (12,000 m.w.) or DYNH (21,000 m.w.). The procedure used was:

Fifty grams of polyethylene and 500 ml. (750 g.) of PCl_3 were charged to a one-liter resin kettle equipped with a stirrer, thermometer, oxygen inlet tube with fritted-glass disperser, and water-cooled condenser connected to a back-up trap and a water trap for absorbing the hydrogen chloride produced during the reaction. Oxygen was passed into the solution through the fritted-glass disperser at a rate of 350-400 ml/minute. The reaction was mildly exothermic. The temperature climbed to 65-70°C and was maintained in this range with a cold-water bath. The polyethylene dissolved in the PCl_3 at 65°C to form a colorless solution which slowly turned yellow as the reaction progressed. The solution became amber colored when a drop in temperature indicated that the reaction was complete (after 5-6 hours).

The reaction mixture was then poured onto crushed ice in a four-liter beaker and agitated with a spatula until the product coagulated. The hydrolysis reaction is quite exothermic and it was often necessary to add more crushed ice to prevent excessive heating. The rubbery product was broken into small pieces and washed six times over a period of two or three days by soaking in fresh water. The product, recovered by filtration, was apparently dry but weighed 700-750 grams.

Samples at this stage of the preparation were insoluble in water and in aqueous sodium hydroxide. When dried over sulfuric acid in a vacuum desiccator, they contained 15-16% phosphorus and about 0.3-0.5% chloride.

The solid rubbery product was then transferred to a wide-mouth jar, loosely capped, and placed in an oven at a temperature of 50°C for 48 hours. During this time, the product slowly changed from a rubbery solid to a jelly-like material and finally to a clear liquid. This liquid was filtered to remove any insolubles present. The resulting clear acidic solution was neutralized either alone or with other materials added to produce fluids for evaluation. After neutralization it was necessary to adjust to the desired viscosity by either adding water or boiling off water at atmospheric pressure.

To prevent the formation of gels rather than solutions upon neutralization, it was necessary that the storage time at 50°C be long enough to result in complete liquefaction.

When large amounts of fluid were required for pump tests, the preparation was scaled up by using 300 gm. of polyethylene and the corresponding amount of phosphorus trichloride (3000 mL) in a four-liter resin kettle. In these larger-scale runs,

temperature was maintained at 65-70°C by regulation of the oxygen flow. Oxygen addition time was 30-35 hours.

A sample of fluid prepared from the clear acidic fluid from 21,000-molecular-weight polyethylene was neutralized to a pH of 8.0 with sodium hydroxide and adjusted to a viscosity of about 30 c.s. at 150°F. In the ASTM Autogenous Ignition Test, no ignition was obtained at temperatures up to 1250°F when either the specified test amount or ten-times the specified test amount was used. The same results were obtained when 1% of sodium dichromate (a promising corrosion inhibitor) was added to the fluid.

A sample of the same fluid had a flash point of >750°F in a micro-flash test apparatus. Some foaming occurred during the heat-up period. The same product was heated rapidly, after evaporation of water, in a porcelain crucible using a Bunsen burner. Charring but no flash or fire occurred. Optical-pyrometer readings indicated that the inside surface of the crucible reached a temperature of 1150°F.

When attempts were made to run ASTM foam test on samples of this fluid, gradual plugging of the diffuser stone occurred. A few tests were completed before pore-plugging became excessive. Data were:

	<u>Foam (ml. after)</u>	
	<u>0 Minutes</u>	<u>10 Minutes</u>
Fluid	490	435
Fluid + 5 ppm Silicone	390	100
Fluid + 10 ppm Silicone	350	10
Fluid + 15 ppm Silicone	350	10

The data indicated that the silicone used (Union Carbide L-530) was somewhat effective in preventing foam formation and caused rapid collapse of the foam. Because foam formation was never a problem in pump tests, no more work on foam suppression was carried out.

Polymers of Unsaturated Acids of Phosphorus

Efforts to produce polymers of esters of unsaturated organic acids of phosphorus having molecular weights high enough to thicken water after hydrolysis and neutralization have been unsuccessful. A summary of these studies follows.

Raw Materials--Because of the deleterious effect of impurities on polymerization reactions, all starting materials were carefully purified by distillation through a one-meter helix-packed column having 42 theoretical plates. Included were trimethyl phosphite, triethyl phosphite, tri-isopropyl phosphite, 1,2-dibromoethane, 1-bromo-2-chloroethane, and allyl bromide.

Synthesis of Vinylphosphonates--Following the directions of Kosolapoff [JACS 70, 197 (1948)] dimethyl, diethyl, and di-isopropyl vinylphosphonates were prepared. After distillation through the one-meter helix-packed column, yields of the desired products were typically about 25%, 45%, and 60% for the methyl, ethyl, and isopropyl esters respectively.

Bis-betachlorethyl vinylphosphonate, obtained from Victor Chemical Co., could not be distilled through the one-meter column. It was purified by distillation under vacuum through a one-foot Vigreux column after addition of a small amount of copper resinate to suppress thermal polymerization.

Data obtained on the vinylphosphonates are:

<u>Ester</u>	<u>Boiling Point</u>	<u>η_D^{20}</u>
Methyl	35-53°C/0.004 mm.	1.4310
Ethyl	91-99°C/13 mm.	1.4292
Isopropyl	99-101°C/21 mm.	1.4245
Betachloroethyl	103°C/0.02 mm.	1.4781

Synthesis of Diethyl Allylphosphonate--Equimolar mixtures of allyl bromide and triethylphosphite were refluxed for 24 hours. The resulting diethyl allylphosphonate was purified by distillation under vacuum through the one-meter helix-packed column. Yields were typically about 90%. The product had η_D^{20} of 1.4329 and boiled at 103-107°C/25 mm.

Polymerization of Vinylphosphonates--In these studies, after the polymerization reaction was completed, unreacted monomer was removed by stripping at pressures below one millimeter using a rotary evaporator partially immersed in a hot-water bath. Where polymerization had occurred, the polymers were viscous colorless to amber liquids.

Esters of vinylphosphonic acids to which 0.1% t-butyl peroxide had been added were held at 135°C for 24 hours. Results were:

<u>Ester</u>	<u>Yield (%)</u>	<u>Molecular Weight</u>
Ethyl	46	1158
Methyl	0	
Isopropyl	0	

Under the same conditions, betachloroethyl in 100 gm. quantities gave a violent exothermic reaction and the product was lost. Betachloroethyl (5 grams) yielded a glassy solid insoluble in organic solvents. These results indicate that the ethyl ester is more readily polymerized than are the methyl or isopropyl esters. The betachloroethyl ester, under these conditions, polymerized readily to form a polymer which, because of its solubility properties, appears to be cross linked.

At lower temperatures, (room temperature to 80°C) no polymerization occurred with the methyl, ethyl, or isopropyl esters when benzoyl peroxide, lauroyl peroxide, or azodiisobutyronitrile were used as polymerization catalysts. With the betachloroethyl ester at 75°C with 0.1% benzoyl peroxide, a small yield of a liquid having a molecular weight of 491 was obtained.

To determine the effect of pressure on the polymerization reaction, the diethyl ester was polymerized at 135°C for 24 hours using 0.1% t-butyl peroxide as catalyst. Results were:

<u>Conditions</u>	<u>Polymer Yield (%)</u>	<u>Molecular Weight</u>
N ₂ at atm. pressure	43	1054
N ₂ at 2600 psi	59	1405
N ₂ at 14,000 psi	74	928

Thus it appears that, although increased pressure led to increased polymer yield, no substantial change in polymer molecule weight occurred.

Other polymerizations of the ethyl ester at 135°C for 24 hours were:

<u>Catalyst</u>	<u>Polymer Yield</u>	<u>Molecular Weight</u>
0.1% t-butyl hydroperoxide	50	1145
Same with N ₂ blanketing	66	1107
0.1% benzoyl peroxide + 0.1% N,N-dimethyl-p-toluidine	0	

Thus t-butylhydroperoxide gave results comparable to those obtained with t-butyl peroxide while the combination of benzoyl peroxide as initiator and N,N-dimethyl-p-toluidine as accelerator was ineffective.

Samples of the ethyl and betachloroethyl esters were mixed with 50% 2,2'-dichlorodiethyl ether (ultra-violet absorber) and irradiated with ultraviolet light for 24 hours at room temperature. Results were:

<u>Ester</u>	<u>Polymer Yield (%)</u>	<u>Molecular Wt.</u>
Ethyl + 0.1% Benzoyl peroxide	34	936
Betachloroethyl	0	
Betachloroethyl + 0.1% Benzoyl peroxide	0	

Thus irradiation does not appear promising as a method for producing high-molecular-weight polymers.

A sample of the betachloroethyl ester, diluted to 50% in 2,2'-dichlorodiethyl ether, was heated at 135°C for 18 hours with 0.1% benzoyl peroxide as catalyst. An additional 0.5% of the peroxide catalyst was added and heating was continued for 24 more hours. An 83% yield of polymer was obtained. Its molecular weight, however, was only 781.

No polymer was obtained when the ethyl ester and the beta-chloroethyl ester were treated, in methylene dichloride solution, with BF_3 -etherate at -60°C and at room temperature. Emulsion polymerization of the betachloroethyl ester at room temperature using a redox catalyst and at reflux temperature using ammonium persulfate as catalyst failed to produce polymer.

Polymerization of Diethyl Allylphosphonate--Attempts to produce high-molecular-weight polymers of diethyl allylphosphonate were unsuccessful. Results obtained may be summarized as follows:

Catalyst	Conditions	Polymer Yield (%)	Molecular Weight
0.1% t-butyl peroxide	135°C , 24 hours	54	1131
0.1% t-butyl peroxide	135°C , 24 hours, 14,000 psi N_2	74	928
0.1% t-butyl hydroperoxide	185°C , 24 hours	27	836
0.1% t-butyl hydroperoxide	185°C , 24 hours, U.V. light	37	862
0.1% t-butyl peroxide	135°C , 24 hours, U.V. light	23	1245
2.0% benzoyl peroxide	50°C , one week	21	1146
0.1% t-butyl hydroperoxide	50% in 2,2'-dichloro-ethyl ether, reflux 24 hours	27	596
0.1% t-butyl hydroperoxide	50% in dimethylformamide, reflux 24 hours	0	
0.1% benzoyl peroxide	50% in dimethylsulfoxide 80°C for 24 hours	0	
1.4 mole % lithium butyl	Room temp., 24 hours Argon atmosphere	0	

At this point, because of unpromising results and because of the promising results being obtained on thickeners from chlorophosphonated polyethylene, attempts to obtain high-molecular-weight polymer of esters of unsaturated acids of phosphorus were abandoned.

TOXICITY OF FIRE-RESISTANT THICKENER

A sample of thickener, prepared from 21,000 molecular-weight polyethylene and neutralized to a pH of 8.0 with sodium hydroxide, was submitted to the International Research and Development Corporation. Results showed that:

1. LD₅₀, administered orally to albino rats was in excess of 10,000 mg./kg.
2. When applied topically to albino rabbits, no evidence of irritation, pharmacotoxicity, or mortality was observed.
3. When instilled into the eyes of albino rabbits, no evidence of irritation occurred.

These results indicated that fluids with thickeners prepared from chlorophosphonated polyethylene should present no undue toxicological hazards under use conditions.

A copy of the complete report from International Research and Development on Compound LF-4581, dated Oct. 15, 1964, is attached.

COMPATIBILITY STUDIES

Early studies on sodium-hydroxide-neutralized products from the chlorophosphonation of polyethylene indicated that compatibility problems with sea water, Buna N rubber, and paint should be minor. However, qualitative corrosion tests, run at room temperature, indicated that it would be necessary to develop a corrosion inhibitor to prevent reaction of the fluid with some of the metals present in the hydraulic system.

Compatibility with Metals--In preliminary tests, samples of sodium-hydroxide-neutralized fluids having pH's below 8.0 (pH paper) attacked iron with the formation of gas (presumably hydrogen) bubbles. At a pH of 8.5 (pH paper) there was no apparent reaction with iron, copper, aluminum, or silver braze. However, rapid attack, with gas-bubble formation, occurred with galvanized iron and with zinc. When all five metals (iron, copper, aluminum, silver braze, and zinc) were present in the same sample at pH 8.5 (pH paper), only zinc was attacked.

A large number of inhibitors and fluid variations were evaluated in screening tests. In these tests, metals, in the form of strips or short lengths of wire, were immersed in the fluid at room temperature. The formation of gas bubbles and/or deposits on the test metals were judged to be evidences of corrosion. The tests were usually continued for at least one week. However, if corrosion occurred, it was always evident no later than 24 hours after the tests were begun.

Table II presents results obtained on samples prepared from four different chlorophosphonation products (two from 21,000 molecular-weight polymer and two from 12,000 molecular-weight polymer) neutralized with sodium hydroxide. These results show that corrosion of iron occurred at pH's (pH paper) below 8. At pH's (pH paper) of 8 and higher the fluids were noncorrosive at room temperature to iron, copper, aluminum, and silver braze, but were quite corrosive to zinc. All four of the products consistently gave the same results. These results showed the need for an effective corrosion inhibitor.

Table III summarizes results obtained in room-temperature screening test aimed at the development of an effective corrosive inhibitor. In all these tests, the fluid used was prepared from 21,000-molecular-weight polyethylene and was neutralized with sodium hydroxide. Of the additive tested, sodium chromate, sodium dichromate, and p-nitrobenzoic acid were considered promising. Sodium molybdate appears to prevent corrosion but some staining of iron, aluminum and zinc occurred.

To further evaluate the effectiveness of promising corrosion inhibitors, static tests were run at 150°F using test strips having 15 sq. cm. surface area immersed in the same sample of fluid. The base fluid was prepared by neutralizing the chlorophosphonation product from 21,000-molecular-weight polyethylene with sodium hydroxide. The data obtained are presented in Table IV. Sodium chromate and sodium

dichromate, effective at room temperature, were effective in minimizing corrosion at 150°F. p-Nitrobenzoic acid, also effective at room temperature, failed to prevent corrosion of aluminum and zinc at 150°F.

Concurrently with studies on corrosion inhibitors, fluid-formula variations were studied in an effort to minimize corrosion. Results obtained are presented in Table V. Only when effective inhibitors (Na_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$, Na_2MoO_4 , or Na_2WO_4) were present were promising results obtained.

Based on the results presented in Table II-V, it was concluded that the optimum pH was 8 (using pH paper) and that the addition of sodium chromate or sodium dichromate at concentration of about one percent (by weight) would minimize the problem of incompatibility with metals present in the submarine hydraulic system.

Compatibility with Sea Water--When 10% of synthetic sea water was added slowly to a stirred fluid prepared by neutralizing product from 21,000 molecular-weight polyethylene with sodium hydroxide at pH of 8 (pH paper) there were no evidences of incompatibility. When synthetic sea water was layered onto the top of the unstirred fluid, a small amount of precipitate formed at the interface. This precipitate disappeared when the mixture was stirred or shaken.

Static corrosion tests were run on samples of a fluid from 21,000-molecular-weight polyethylene neutralized with sodium hydroxide to a pH of 8.5 (pH paper) containing corrosion inhibitors. Tests were run with and without the addition of 11% synthetic sea water. Weight-loss data, after eleven days at 150°F, are:

Inhibitor	Weight Loss (mg. from 15 cm ² surface area)			
	Fe	Zn	Al	Cu
1% $\text{Na}_2\text{Cr}_2\text{O}_7$ **	+0.4	1.7	Mil	0.1
1% $\text{Na}_2\text{Cr}_2\text{O}_7$ +11% synthetic sea water	0.2	3.6	0.2	+0.2
1% p-nitrobenzoic acid (pH -8)**	0.3	73.4	87.1	1.3
1% p-nitrobenzoic acid + 11% synthetic sea water	0.1	187.5	+142.9*	1.0

* Heavy insoluble deposit.

** Data also presented in Table IV.

These data indicate that contamination with sea water should not greatly increase corrosion when an effective chromate-type corrosion inhibitor is present. When an ineffective inhibitor, p-nitrobenzoic, was present, contamination with sea water appeared to accelerate zinc and aluminum corrosion.

Compatibility with Buna N--Samples of fluid from 21,000-molecular-weight polyethylene neutralized to a pH of 8.0 (pH paper) with sodium hydroxide were placed in screw-cap jars. A Buna N "O" ring, obtained from Precision Rubber Co., was placed in each jar. The jars were loosely capped and stored at 150°F for seventy hours. At the end of this time, comparison with new rings indicated no swelling, cracking, or loss of elasticity. After one week at 150°F, there was no evidence of change in a test strip of Buna N (Precision Rubber Co.) immersed in the same fluid to which 1.0% sodium chromate had been added. Iron, copper, aluminum, and zinc strips were also immersed in the fluid throughout the test to show that, in the presence of metals, changes in the fluid detrimental to compatibility with Buna N would not take place.

Compatibility with Painted Surfaces--When fluid of pH-8 (pH paper) from 21,000-molecular-weight polymer was allowed to dry for several days on painted-metal furniture and on vinyl floor tile, the residue could be washed off with water or scraped off with no indication of surface damage.

Pour-Depressor Development

Fluid prepared from 12,000 and 21,000 molecular-weight polyethylene by chlorophosphonation and neutralization were found to have pour points of about +28°F to +30°F. Work aimed at the development of an appropriate pour depressor was therefore carried out. Studies showed that pour point could be lowered to 0°F by the addition of about 25% of ethylene glycol or of about 30% of glycerin or diethylene glycol. Because it is likely that use of these compounds as pour depressors would have adverse effects on flammability characteristics, studies were aimed at the development of pour depressors having flame-resistant properties. Several alkane phosphonic acids were prepared for evaluation, in the form of alkali metal salts, as pour depressors.

Preparation of Alkane Phosphonic Acids--These acids were prepared by refluxing the corresponding esters with concentrated hydrochloric acid (mole ratio HCl/ester = 3.0) for 24 hours. At the end of the reflux period, water, HCl, and alkyl halide were removed by evaporation using a rotary evaporator. Methanephosphonic acid had a melting point of 103-108°C which increased to 108-110°C after recrystallization from methyl ethyl ketone. Ethanephosphonic acid melted at 57-60°C and at 61-63°C after recrystallization from diethyl ether. Butane phosphoric acid was a white solid (melting point not determined) and 2-ethylhexanephosphonic acid was a viscous brown liquid.

Alkali Metal Phosphonates as Pour Depressors--A few tests were carried out to evaluate alkali metal salts of the phosphonic acids as freeze-point depressors in the water. Results were:

<u>Con- centration</u>	<u>Salt</u>	<u>Freezing Point (°F)</u>
1.0 molar	Sodium methanephosphonate	+23
2.0 molar	Sodium ethanephosphonate	+7
1.5 molar	Potassium ethanephosphonate	+14
2.0 molar	Potassium ethanephosphonate	+2
2.5 molar	Potassium ethanephosphonate	-18 -18
2.5 molar	Potassium methanephosphonate	-6
2.5 molar	Potassium butanephosphonate	-27

These results indicated that these salts may be useful as pour depressors.

Ethanephosphonic acid in amounts calculated to yield the desired concentrations of the sodium salt was added to the acidic solution from the chlorophosphonation of 21,000-molecular-weight polyethylene. The solutions were neutralized to pH-8 (pH paper) with sodium hydroxide. The fluids were then adjusted to the desired viscosity by addition of or boiling-off of water and the addition of more ethanephosphonic acid or acidic thickener solution and sodium hydroxide. Pour-point data were:

<u>% Sodium Ethanephosphonate</u>	<u>Pour Point (°F)</u>	<u>Cloud Point (°F)</u>
10	20	20
15	20	25
20	30	70

These results show that sodium ethanephosphonate is relatively ineffective as a pour depressor because of insufficient solubility.

The same procedure was repeated using acidic solution from the chlorophosphonation of 12,000-molecular-weight polyethylene and potassium hydroxide instead of sodium hydroxide. Pour-point data were:

<u>% Potassium Ethanephosphonate</u>	<u>Pour Point (°F)</u>	<u>Cloud Point (°F)</u>
0	+40	
13	-15	-10
18	-40	-40
23	-26	-24
26	-25	-
30	-18	-15

These data show that, in fluids containing potassium-hydroxide-neutralized thickener, potassium ethanephosphonate is an effective pour depressor. The optimum concentration of potassium ethanephosphonate in this fluid appears to be near 18%.

Viscosity and Shear Stability

Early in the program, it was found that fluids having viscosities in the range of 25-31 cs. at 150°F could be formulated using thickeners produced from 12,000-molecular-weight and 21,000-molecular-weight polyethylene by chlorophosphonation, hydrolysis, aging, and neutralization. It was difficult to determine the exact amount of thickener required because the thickener as such was not isolated and because small changes in pH caused large changes in viscosity. It appeared, however, that generally about 17% and 20% thickener from 21,000-molecular-weight polymer and 12,000-molecular-weight polymer respectively was required. Because of high pour points, viscosities at 25°F could not be obtained on these fluids until effective pour depressors were found.

Shear Stability--Samples prepared from 21,000- and 12,000-molecular-weight polyethylene were neutralized to a pH of 8.0 (pH paper). The resulting products were tested for viscosity loss in the Raytheon Sonic Oscillator at 10,000 cycles, 0.7 R.F. amperes at 100°F for 30 minutes. Results were:

<u>Polymer Molecular Weight</u>	<u>Viscosity (c.s. at 150°F)</u>	
	<u>Before</u>	<u>After</u>
21,000	24.2	25.7
12,000	17.4	17.6

These data indicated that no viscosity loss occurred. They were, however, later found to be misleading, probably because the viscosities of the sheared sample had been obtained about 24 hours after shearing had occurred.

A Vickers Vane pump test was run at 150°F and 1,000 psi on a fluid prepared from 21,000-molecular-weight polymer neutralized with sodium hydroxide to a pH of 8.0 (pH paper). One percent of sodium chromate was present as a corrosion inhibitor. At the end of 20 hours, the fluid had decreased in viscosity at 150°F from 30.0 cs to 22.3 cs. Because of these results, further sonic-shear data were obtained:

<u>Polymer Molecular Weight</u>	<u>Viscosity (cs. at 150°F)</u>	
	<u>Before</u>	<u>After</u>
21,000 (pump test fluid)	30.0	23.1
21,000	39.5	35.6
12,000	31.1	29.7

In these tests, viscosities were determined immediately after shear and serious losses in viscosity were obtained with the 21,000-molecular-weight product.

A retained sample of the pump-test fluid showed a viscosity of 25.4 cs. at 150°F. The same fluid had a viscosity of 30.0 cs. at 150°F at the beginning of the pump test. Samples of sheared and unsheared fluid from 21,000-molecular-weight polymer were therefore allowed to stand undisturbed for 9 days. Viscosity data were:

<u>Sample</u>	<u>Viscosity (cs. at 150°F)</u>	
	<u>Immediately</u> <u>After Shearing</u>	<u>After</u> <u>9 Days</u>
Unsheared	39.5	46.8
Sheared (1)	35.6	43.9
(2)		42.2
(3)		41.2

The three viscosities reported on the sheared fluid after nine days were those obtained by sucking the fluid back into the viscosimeter tube and rerunning.

Thus the viscosity of this fluid was dependent on its previous history, possibly because of varying degrees of loose bonding between thickener molecules because of attractive forces between the large number of phosphonate groups.

A large batch of fluid was prepared for pump testing which contained about 20% of thickener prepared from 12,000-molecular-weight polyethylene, 18% of potassium ethanephosphonate and 1.4% potassium chromate. pH was 8.0 to pH paper. Data obtained by the sonic shear test were:

<u>Fluid</u>	<u>Viscosity (cs. at 150°F)</u>	
	<u>Immediately</u> <u>After Shearing</u>	<u>After</u> <u>10 Days</u>
Unsheared	30.4	32.4
Sheared	29.0	29.6

Although some viscosity loss occurred in the shear test and some increase in viscosity occurred on standing, the viscosity-stability properties were improved over those of fluids containing higher-molecular-weight thickener and no potassium ethanephosphonate.

Viscosity at 25°F--Viscosity data obtained on the pump-test fluid containing potassium-hydroxide-neutralized thickener and potassium ethanephosphonate were:

<u>Viscosity at</u>					
<u>150°F</u>		<u>100°F</u>		<u>25°F</u>	
<u>SSU</u>	<u>CS</u>	<u>SSU</u>	<u>CS</u>	<u>SSU</u>	<u>CS</u>
144	30.4	377	81.4	9768	2118

The viscosity of this batch of fluid was at the upper end of the desired range (25-31 cs) at 150°F and much higher than the desired maximum (850 cs) at 25°F. The measured viscosity at 25°F was considerably higher than would be expected by extrapolation from data at 150°F and 100°F.

This fluid, and all fluids discussed earlier in this report, were neutralized to the pH value reported using pH paper. When a fluid, containing ethanephosphonic acid and thickener (12,000 m.w. polymer), was neutralized to a pH of 8.0 using pH paper, it was found that its actual pH, measured on two different pH meters, was about 10. Fluids neutralized to a pH of 8.0 on the meter showed pH's of about 6.0 on pH paper. Thus it appears that, in the range of interest, there is a constant difference of about 2 pH units between results obtained with pH paper and with the meter. It is also obvious that fluids which had been evaluated earlier were more alkaline than had been recognized.

A sample of fluid was prepared by neutralizing a blend of thickener from 12,000-molecular-weight polymer and ethane-phosphonic acid (17%) with potassium hydroxide to a pH of 7.4 on the pH meter. Viscosity data obtained were:

<u>Viscosity (cs. at 150°F)</u>	<u>Viscosity (cs. at 25°F)</u>
23.2	566

Although the viscosity at 150°F was somewhat below the desired range (25-31 cs.), the viscosity at 25°F was low enough to indicate that a reduction in pH would allow formulation of fluids which had satisfactory low-temperature viscosity.

Ability to Lubricate

In service, submarine hydraulic fluids are required to lubricate ball bearings and screw pumps at pressures approaching 5 000 psi. Because such equipment was not available in this laboratory, Vickers Vane pump tests were run to gain some insight on the lubricating ability of the fluids under study. In early pump tests, extremely high ring wear was obtained. It was therefore thought necessary to develop an appropriate antiwear additive. Although results obtained in the Shell four-ball test are recognized to give poor correlation with vane-pump-test results, the Shell test was used as a screening test because it is a short-time test and requires only a small test sample.

Shell Four-Ball Tests--In the study on antiwear additives, early tests were run for one hour at 1800 rpm, room temperature, with a 15 kg. load. The base fluid was prepared by neutralizing a mixture of thickener from 12,000-molecular-weight polymer and ethanephosphonic acid with potassium hydroxide to a pH of 8.0 with pH paper. Table VI presents the data obtained. All of the additives tested were ineffective in this test.

At this time, because most of the wear obtained in the Shell four-ball test took place early in the test, the test period was decreased for one hour to one-half hour. Data obtained on one-half-hour tests are presented in Table VII. The results show that the addition of Duomeens (long-chain alkyl derivatives of 1,3-diaminopropane) and sucrose cause some reduction in wear-scar diameters.

Because it was thought that replacement of some of the water in the fluid with glycerin might lead to increased lubricating ability, Shell four-ball tests were run on fluids containing glycerin. The data, shown in Table VIII, indicated that the addition of large amounts of glycerin tended to decrease scar diameter somewhat. The results of the last two tests indicated that the addition of potassium chromate as a corrosion inhibitor may have an adverse effect on wear.

At this time, because (1) the presence of high concentrations of organic hydroxyl compounds (glycerin and sucrose) seemed to result in somewhat lower wear, and (2) because replacement of ethanephosphonic acid (a dibasic acid) with a monobasic acid might lead to more desirable viscosity properties, tests were carried out with fluids containing bis-hydroxymethylphosphonic acid (Hooker Chemical Co.) instead of ethanephosphonic acid. Because the hydroxymethyl acid has a higher molecular weight and produces fewer ions, 30% of the acid was used. With this acid, to obtain the desired viscosity, it was necessary to raise the thickener concentration from about 20% to about 25%. This may have resulted because of the absence of the buffering action exhibited by the ethanephosphonic acid.

Table IX presents the Shell four-ball data obtained when ethanephosphonic acid was replaced by bis-hydroxymethylphosphonic acid. The data show that the acid change resulted in a reduction in wear-scar diameter. The remaining tests show that, of several possible corrosion inhibitors tested, sodium chromate, sodium dichromate, and sodium vanadate caused increased wear-scar diameter.

Vickers Vane Pump Tests--A total of ten pump tests were carried out during this study. All tests were run at 150°F, 1000 psi, and a delivery rate of about 1.5 gallons/minute. Fluid samples were withdrawn periodically for viscosity determinations. Table X summarizes the weight-loss data obtained in these tests.

TEST NO. 1: This test was run on a fluid containing about 17% of thickener prepared from 21,000-molecular-weight polymer neutralized to a pH of 8.0 (pH paper) with sodium hydroxide, 1.0% sodium dichromate, and 5 ppm of Union Carbide L-530 (a silicone-type foam suppressor). Delivery rate was 1.9 gal./min. rather than 1.5 gal./min. rate in later tests. As shown in Table X, excess wear occurred, particularly on the ring. Viscosity loss was excessive but there was no substantial change in pH. Data were:

	Viscosity (cs. at 150°F)	(pH paper)
Initial	30.0	8.0
After test	20.0	8

TEST NO. 2: The fluid used in this test contained about 20% of potassium thickener from 12,000-molecular-weight polymer, 18% of potassium ethanephosphonate, 1.4% potassium chromate, and 5 ppm of L-530 silicone. The fluid had a pH of 8.0 measured with pH paper. This was the fluid which exhibited the viscosity instability and poor low-temperature viscosity discussed earlier in this report.

Two gallons of this fluid were charged to the sump of the pump. After ninety hours of operation, excessive water loss had occurred because of evaporation resulting from a poorly fitted sump cover. At this time, the fluid was examined and found to have a viscosity of 109 cs. at 150°F. Sufficient water was added to bring the viscosity down to about that of the original fluid (30.4 cs. at 150°F). Total volume of the fluid which resulted was about 2.75 gallons. Thus, unlike the results obtained in Test No. 1, there was a substantial increase in viscosity resulting from the shearing action of the vane pump.

New pump parts were installed and the test was continued for an additional 140 hours. Because of evaporation loss, it was necessary to add about 1 1/2 pints of water every twenty-four hours. No apparent increase in total volume occurred and the viscosity returned to about that of the original fluid after each water addition.

As shown in Table X, excessive wear occurred. Weight losses were similar to those obtained in Test No. 1.

TEST NO. 3: This test was run on the used fluid from Test No. 2 to which 1% of isopropyl-butyl dithiophosphoric acid had been added. The test was discontinued at 79 hours because pressure could no longer be maintained. As shown in Table X, weight losses were high and there was evidence of severe brass-end-plate corrosion.

TEST NO. 4: Before this test was started, the sump cover plate was redesigned so that water loss by evaporation would be minimized. In this test, the fluid contained about 20% of potassium thickener and 1% potassium chromate. Thirty percent of glycerin was used as pour depressor instead of potassium ethanephosphonate. The fluid had a pH of 8.0 to pH paper and a pH of 10.0 when measured with a pH meter. Because of the poor lubricity properties of silicones and because foaming had been no problem in earlier tests, no antifoam agent was added.

As was the case with the fluid containing potassium ethanephosphonate (Test No. 2), viscosity increased rapidly during the early part of the test. Data are:

<u>Viscosity (cs. at 150°F)</u>	
Initial	31.7
After 20 hours	60.8

It was necessary to add about 1200 ml. of water at this point to bring the viscosity down to about that of the original fluid. The viscosity continued to rise at a somewhat slower rate throughout the test and it was necessary to add a total of 1250 ml. of water throughout the remainder of the test to maintain the original viscosity.

As shown in Table X, weight loss in this test was excessive. There were however, no indications of foaming problems during the test.

TEST NO. 5: This test was run using the used fluid from Test No. 4 to which 1.5% of Aqua-Dag colloidal graphite was added. The data in Table X show that this additive had no substantial effect on pump wear. Here again, the viscosity increased substantially; it was necessary to add a total of about 1250 ml. of water to maintain the fluid at about its original viscosity.

TEST NO. 6: This test was run on a fluid containing potassium thickener from 12,000-molecular-weight polymer, 25% potassium ethanephosphonate, and 1.0% molybdic acid. The fluid had a pH of 7.4 when measured on a pH meter.

This fluid performed in a much more satisfactory manner than did earlier fluids. Weight loss data, shown in Table X, indicate that very little wear occurred except on the ring. Ring wear was reduced from the 10-18 gram level of earlier tests to about 3.4 grams. Viscosity increased slightly during the test because of some water loss, estimated to be about 400 ml., by evaporation. Viscosity data were:

<u>Viscosity (cs. at 150°F)</u>	
Initial	25.1
After test	28.0

TEST NO. 7: This test was run on the used fluid from Test No. 6 with the pH increased by the addition of potassium hydroxide to 9.4 when measured with the pH meter. Results, shown in Table X, generally were similar to those of Test No. 6. Although ring weight loss was somewhat lower, rotor and vane weight losses were substantially higher than on the same fluid at a lower pH. Viscosity data were:

Viscosity (cs. at 150°F)

Initial	25.5
After test	28.7

TEST NO. 8: In this test, potassium bis-hydroxymethylphosphonate was used in place of potassium ethanephosphonate as the pour depressor. The fluid was prepared by neutralizing a mixture of acidic thickener from 12,000-molecular-weight polymer, and bis-hydroxymethylphosphonic acid with potassium hydroxide to a pH of 8.0 on the pH meter. After viscosity adjustment the fluid contained about 25% bis-hydroxy-methylphosphonic acid (about 30% of the potassium salt). One percent of molybdic acid was added to the fluid before neutralization. Because it was necessary to boil off water to achieve the desired viscosity, the potassium molybdate content of the final fluid was about 2%.

Weight-loss data, reported in Table X, show that quite low losses occurred on the vanes and rotor. Ring weight loss was 0.34 grams. This loss is much less than was obtained in earlier tests. Viscosity data were:

Viscosity (cs. at 150°F)

Initial	25.4
After test	32.0

Here again some water was lost by evaporation during the test.

After this run was completed, inspections and static corrosion tests at 150°F were run. Data were:

	<u>Before Test</u>	<u>After Test</u>
Viscosity (cs. at 150°F)	25.4	-
Viscosity (cs. at 25°F)	633	-
Pour (°F)	-50	-
Corrosion (mg/sq. cm., 7 days)		
Fe	0.07	Nil
Zn	0.36 (gain)	0.70 (gain)
Al	0.01 (gain)	0.10
Cu	0.02	0.15 (gain)
Ag braze	Nil	Nil

Other than a very slight indication of deposit on the zinc strips, no corrosion problems were evident.

TEST NO. 9: This test was run on a batch of fluid formulated in the same way as that run in Test No. 8. Two quarts of this fluid were submitted in partial fulfillment of the contract requirements. Weight-loss data, in Table X, show that somewhat high weight loss on the ring occurred (1.37 gm. compared with 0.34 gm. in Test No. 8). Rotor and vane weight losses were satisfactorily low. Viscosity data were:

Viscosity (cs. at 150°F)

Initial	30.2
After test	34.4

During this test, one-inch-square test specimens obtained from Robert K. Johnson, San Antonio, Texas, were immersed in the fluid in the sump. Weight-loss data were:

<u>Test Strip</u>		<u>Weight</u>
<u>Type</u>	<u>Specification</u>	<u>Loss (mg.)</u>
Silver Braze	Mil-B-15395A Grade IV	Nil
Aluminum	QQ-A-250/46	Nil
Bronze (cast)	Mil-B-16541A (WEP)	Nil
Phosphor Bronze	QQ-B-750, Comp. A	Nil
Copper	QQ-C-5766	Nil
Nickel-Copper (Monel 400)	QQ-N-281, Class A	0.5 (gain)
Steel	QQ-S-698-FS 1009	0.8
Galvanized Steel	Steel (QQ-S-698-FS 1009)	3.2
	Zinc electroplated per	
	QQ-Z-325a, Type II,	
	Class 1	

At the end of the 72-hour test period, there was slight evidence of corrosion of zinc on the galvanized steel. There were no other evidences of corrosion.

TEST NO. 10: This test was a 72-hour continuation of Test No. 9 with new pump parts. Water (300 ml.) was added to the used fluid from Test No. 9 to lower viscosity to the desired level. Weight-loss data, shown in Table X, were substantially similar to those obtained in the first test on this fluid. Viscosity data were:

Viscosity (cs. at 150°F)

Initial	28.3
After test	31.7

Throughout this test, two Buna N rubber "O" rings and one test strip (from Goshen Rubber Co.) were suspended in the fluid in the sump. At the end of the test, there were no indications of cracking or loss of elasticity. Swell data, obtained by the weight-in-water/weight-in-air procedure were:

	<u>% Swell</u>
"O" ring No.1	+0.21
"O" ring No.2	+0.11
Average	+0.16

"Best Effort" Formulation

Based on the work reported herein, the fluid which most closely meets the requirements for a successful fluid contains water, potassium-hydroxide-neutralized thickener prepared by chlorophosphonation of 12,000-molecular-weight polyethylene, potassium bis-hydroxymethylphosphonate as pour depressor, and potassium molybdate as corrosion inhibitor. The pH of the fluid is about 8 measured on a pH meter. Based on calculations from the starting materials used, the approximate formula is:

27% Potassium thickener
30% Potassium bis-Hydroxymethylphosphonate
2% Potassium Molybdate
41% Water

It should be possible to decrease the amount of the pour depressor and still meet the 0°F pour requirements. Because of time limitations, however, evaluations on such fluids were not carried out.

Comparisons of the properties of this fluid with those desired follow:

Fire-Resistance--The following data were obtained:

	<u>Desired</u>	<u>This Fluid</u>
Flash (°F)	450 min.	640+
Fire (°F)	550 min.	640+
AIT (°F)	900 min.	1450+

It was difficult to determine flash and fire points on this fluid because of foaming which began at about 280°F. Apparently, up to this temperature considerable tightly held water remains in the fluid. After several hours of careful heating and stirring at 280-300°F, the residue became solid. No flash or fire occurred during this heating period or when the residue was heated to 640°F.

The sample for autogenous ignition temperature was prepared by boiling off water at 220-230°F until bubbling ceased. The residue was an extremely viscous liquid at 220-230°F. A somewhat modified ASTM procedure was used. Comparative AIT's using the same equipment and procedure were:

	<u>AIT (°F)</u>
Fluid Residue	1450+
Glycerin	900
Diethylene glycol	890

Viscosity and Pour--Typical data are:

	<u>Desired</u>	<u>This Fluid</u>
Viscosity (cs. at 150°F)	25-31	30.2
Viscosity (cs. at 25°F)	850 max.	659
Pour (°F)	0 max.	-50
Cloud Point (°F)	-	-50

Shear Stability--A sample of fluid was tested for shear stability with the following results:

	<u>Viscosity (cs. at 150°F)</u>
Before Shear	24.2
Immediately After Shear*	23.8

* In Raytheon Sonic Oscillator at 10,000 cycles, 0.7 R.F. Amperes, at 100°F for 30 minutes.

Although the viscosity of this sample was slightly low, the data indicate that the fluid has satisfactory shear stability.

Specific Gravity---Data are:

	<u>Optimum</u>	<u>Maximum</u>	<u>This Fluid</u>
Specific Gravity 1.0-1.2		1.6	1.4

This fluid has a specific gravity above the optimum range but below the maximum desired.

Lubricating Ability--Pump-test data, presented earlier in this report, indicate that this fluid has some lubricating ability. It may be necessary, however, to improve the lubricity and antiwear properties of the fluid before satisfactory lubrication of the pump and bearings in the submarine hydraulic system can be achieved.

Compatibility--Static-corrosion-test data and data obtained on test specimens suspended in the fluid during the pump test on this fluid indicate that no corrosion problems with metals should occur. Results are presented earlier in this report.

Test data, presented earlier in this report, indicate no compatibility problems with Buna N rubber.

A metal panel was painted with JAN-P-700 alkyl paint. The paint was allowed to dry at room temperature for twenty-four hours. A portion of the painted surface was covered with the fluid and the panel was stored at 140°F for 20 hours. The residue was washed off with water and light swabbing. There was no apparent damage except a light-yellow stain which did not wash off. It may have been very slightly easier to scratch the paint which had been in contact with the fluid than to scratch the paint which had not been in contact with the fluid.

When 10% of synthetic sea water is added to this fluid, a small amount of precipitate is formed. When the mixture is stirred or shaken, the precipitate dissolves.

Stability During Storage and Use--Samples of this fluid have been maintained at the boiling point for several hours for water removal to increase viscosity to the desired level. No changes in properties, other than viscosity, have resulted and there was no evidence of separation or precipitation. No precipitation or cloud formation occurred when the fluid was cooled to its pour point (-50°F). A sample of the fluid was filtered through five-micron millipore paper. There was no apparent deposit on the paper or slow-down in the rate of filtration. Throughout the Vickers Vane pump tests reported herein, the fluid was pumped through two ten-micron filters. No undue amount of deposits were built up on the filters and no filter plugging occurred.

Foaming--Early in this study it was shown that foaming of the fluid could be controlled by the addition of a silicone-type foam suppressor. However, because foaming was never a problem in pump tests, no foam suppressor was included in the final formulation.

Toxicity--Preliminary toxicological studies show the thickener used to be substantially nontoxic. The report of this study, carried out by the International Research and Development Corporation, is attached. Toxicological studies are being carried out on the final formulation and the report will be issued as an addendum to this report.

Fluid Residues--Fluid residues are easily removed by flushing with water. After lengthy drying, light swabbing hastens residue removal with water.

TABLE I

CHLOROPHOSPHONATION REACTIONS

Material	Amount of Material, g	Amount PCl ₃ , g	Duration of Run, hrs.	
Polyethylene DYLt, (12,000 MW)	25	475	6.0	Darkened and gelled in removing POCl ₃ - No further work-up.
Polyethylene DYLt, (12,000 MW)	25	475	6.0	Gel after week in 1500 ml water, light yellow.
FRS 1500 Rubber	50	475	-	No reaction.
Polyethylene Grease (1200 MW)	50	475	4.0	Eventually went into solution in water after two weeks.
Polyethylene Grease (1200 MW)	25	475	3.0	Gel which eventually went into solution.
Paraffin Wax (152.5°F MP)	50	475	3.0	Off-white material resembling soft putty.
Polyethylene DYDT (4000 MW)	50	750	6.0	Light amber solution obtained after day in oven at 50°C (741 g).
Paraffin Wax (152.5°F MP)	50	750	6.0	Most of material was lost in washing.
Polybutene L-50	50	750	6.0	Black oily material - insoluble in water.
Polybutene H-1900	50	750	3.0	Very viscous and stringy - insoluble in water.
Paraffin Wax (152.5°F MP)	50	750	3.0	Lost most of product in washing - Aqueous viscous brown solution.
Polyethylene DYLt (12,000 MW)	50	750	2.5	Amber viscous fluids at 10% concentration in water.
Polyethylene DYDT (4000 MW)	50	750	3.0	Amber solution at 12% concentration in water.
Polyethylene DYLt (12,000 MW)	100	375	4.0	Would not go into solution - Hard white solids.
Polyethylene DYDT (4000 MW)	100	375	4.0	Hard solid - Would not go into solution.
Polyethylene Grease (1200 MW)	50	525	2.0	Dark brown stringy material - Incompatible with water.
Polyethylene DYDT (4000 MW)	50	525	2.0	Amber solution at 12% concentration in water.
Polyethylene DYNH (21,000 MW)	50	750	5.0	Viscous amber solution at 10% concentration in water.
Polyethylene Grease (1200 MW)	50	750	5.0	POCl ₃ replaced with chlorobenzene solvent - insoluble in chlorobenzene
Polyethylene DYNH (21,000 MW)	50	750	6.0	Viscous solution at 10% concentration in water.
Mineral Seal Oil	50	750	6.0	No reaction
Polyethylene DYNH (21,000 MW)	50	750	5.0	Amber viscous solution at 10% concentration in water.

TABLE II

CORROSION TESTS AT ROOM TEMPERATURE

Test Conditions: All metals in same sample of fluid.

Test Duration: One week or longer.

Results Code: O = no evidence of corrosion
G = gas bubble formation
D = deposit formation

<u>Formulation</u>		<u>Results</u>				
<u>Polymer m.w.</u>	<u>pH (pH paper)</u>	<u>Fe</u>	<u>Zn</u>	<u>Al</u>	<u>Cu</u>	<u>Ag Braze</u>
21,000	ca. 7	G	-	-	0	0
21,000	<8	G	-	-	0	0
21,000	7.5	G	GD	G	0	0
21,000	8.5	0	-	-	0	0
21,000	8.0	0	GD	0	0	0
21,000	8.5	0	GD	0	0	0
21,000	8.5	0	GD	0	0	0
21,000	8.5	0	GD	0	0	0
21,000	8.5	0	GD	0	0	0
21,000	9.5	0	GD	-	0	0
12,000	8.0	0	GD	0	0	0
12,000	8.0	0	GD	0	0	0
12,000	8.5	0	GD	0	0	0
12,000	8.5	0	GD	0	0	0

TABLE III

CORROSION TESTS AT ROOM TEMPERATURE--ADDITIVES

Test Condit : All Metals in same sample of fluid.

Test Durati : One week or longer.

Results Code.
 O = no evidence of corrosion
 G = gas-bubble formation
 D = deposit formation
 S = stain
 Sl = slight

Formulation		Results				
Additive	pH (pH paper)	Fe	Zn	Al	Cu	Ag Braze
None	7.5	G	GD	G	O	O
None	8.0	O	GD	G	O	O
1.0% Na ₂ CrO ₄	8.0	O	O	O	O	O
1.0% Na ₂ Cr ₂ O ₇	8.0	O	O	O	O	O
1.0% Na ₂ Cr ₂ O ₇	8.5	O	O	O	O	O
2.0% Na ₂ Cr ₂ O ₇	8.5	O	O	O	O	O
1.0% Na ₂ Cr ₂ O ₇	9.0	O	O	O	O	O
5.0% Na ₂ CrO ₄	8.0	O	O	O	O	-
2.0% Na ₂ Cr ₂ O ₇ + 1.0% Triethanolamine	8.0	O	O	O	O	-
1.0% Na ₂ Cr ₂ O ₇ + 0.5% Triethanolamine	8.0	O	O	O	O	-
1.5% Na ₂ Cr ₂ O ₇ + 0.3% Triethanolamine	-	O	O	O	O	O
1.0% Na ₂ MoO ₄	8.0	O	O	O	O	-
5.0% Na ₂ HPO ₄	8.0	O	SlG	O	O	-
1.0% Na ₂ HPO ₄	8.5	SlS	SlS	SlS	O	-
1.0% NaNO ₂	8.0	O	G	O	O	O
1.0% Borax	8.0	S	G	O	O	-
1.0% Borax + 0.1% Thiourea	7.5	G	G	G	O	O
1.0% Borax + 0.1% Thiourea	7.0	O	G	O	O	-
1.0% Borax + 0.1% Thiourea	8.0	O	G	O	O	-
1.0% Borax + 0.5% Na Mercaptobenzothiazole	8.0	O	G	O	O	-
1.0% Benzoic Acid	8.0	O	G	O	O	-
1.0% Salicylic Acid	8.0	O	G	O	O	-
1.0% Salicylic Acid	7.2	O	G	O	O	-
1.0% o-Nitrobenzoic Acid	8.0	O	G	-	O	-
0.5% o-Nitrobenzoic Acid	7.5	GD	GD	O	O	-
1.0% o-Nitrobenzoic Acid	7.5	GD	GD	O	O	-
0.5% o-Nitrobenzoic Acid	8.2	D	D	O	O	-
0.25% o-Nitrobenzoic Acid	8.2	S	S	O	O	-
1.0% o-Nitrobenzoic Acid	8.0	S	S	O	O	-
2.0% p-Nitrobenzoic Acid	9.0	O	O	O	O	-
2.0% p-Nitrobenzoic Acid	8.5	O	O	O	O	-
2.0% p-Nitrobenzoic Acid	12+	O	O	S	O	-

TABLE III (cont'd.)

Formulation		Results					
Additive	pH (pH paper)	Fe	Zn	Al	Cu	Ag	Braze
1.0% p-Nitrobenzoic Acid	8.0	0	0	0	0	-	-
1.0% p-Nitrobenzoic Acid	8.5	0	0	0	0	-	-
0.5% p-Nitrobenzoic Acid	8.0	0	D	0	0	-	-
1.0% p-Nitrobenzoic Acid + 0.1% Na ₂ CrO ₄	8.0	0	0	0	0	-	-
1.0% p-Nitrobenzoic Acid + 0.1% Thiourea	8.2	0	0	0	S	-	-
1.0% p-Nitrobenzoic Acid + 0.3% Na Mercaptobenzothiazole	8.0	0	0	0	0	-	-
1.0% p-Nitrobenzoic Acid + 1.0% Triethanolamine	8.5	0	D	0	0	-	-
1.0% p-Nitrobenzoic Acid + 1.0% Borax	8.0	0	0	0	0	-	-
1.0% p-Nitrobenzoic Acid + 10.0% Na ethanephosphonate	8.0	0	0	0	0	-	-
3.0% Triethanolamine	8.0	0	G	G	0	-	-
1.0% Triethanolamine	8.0	0	G	G	0	-	-
0.5% Triethanolamine	8.5	0	G	-	0	-	-
0.1% Triethanolamine	9.0	0	G	-	0	-	-
1.0% Morpholine	8.0	0	GD	G	0	-	-
1.0% Propylene oxide	8.0	-	GD	G	0	-	-
1.0% Propylene oxide + 0.5% Morpholine	8.0	SIS	G	0	0	-	-
0.1% Thiourea	8.0	0	GD	0	0	-	-
1.0% Na Mercaptobenzothiazole	8.0	0	SG	SG	0	-	-
1.0% Dimercaptothiadiazole	8.5	S	G	G	0	-	-
1.0% Oleylcitrimic Acid	7.2	0	SG	SG	0	-	-
0.5% Oleylcitrimic Acid + 1.0% Triethanolamine	8.0	0	0	G	0	-	-
1.0% Nalco 390	8.0	G	G	G	0	-	-

TABLE IV
STATIC CORROSION TESTS

Test Conditions: 150°F, 11 days, 15 cm² area of test strips.

<u>Formulation</u>		<u>Weight Loss (mg.)</u>			
<u>Inhibitor</u>	<u>pH (pH paper)</u>	<u>Fe</u>	<u>Zn</u>	<u>Al</u>	<u>Cu</u>
1.0% Na ₂ Cr ₂ O ₇	7.5	0.5	2.4	3.2	0.3
1.0% Na ₂ Cr ₂ O ₇	8.0	nil	2.3	0.4	0.5
1.0% Na ₂ Cr ₂ O ₇	8.5	+0.4	1.7	nil	0.1
1.0% Na ₂ Cr O ₄	8.0	0.1	1.9	1.0	0.2
1.0% Na ₂ Cr O ₄ + 1.0% Borax	8.0	nil	1.5	0.7	+0.1
1.0% p-Nitrobenzoic Acid	8.0	0.3	73.4	87.1	1.3
2.0% p-Nitrobenzoic Acid	8.0	0.9	38.6	73.8	1.3
5.0% p-Nitrobenzoic Acid	8.0	+0.3	46.2	55.6	1.8
1.0% p-Nitrobenzoic Acid	9.0	Heavy gas evolution and precipitation			
1.0% p-Nitrobenzoic Acid + 1.0% Borax	8.0	1.6	55.9	32.0	1.5
1.0% p-Nitrobenzoic Acid + 1.0% Na ₂ Cr ₂ O ₇	8.0	0.4	1.5	0.7	+0.1

TABLE V

CORROSION TESTS AT ROOM TEMPERATURE--FLUID MODIFICATIONS

Test Conditions: All metals in same sample of fluid

Abbreviations: pH's were measured with pH paper.
TEA = Triethanol amine.
PO = Propylene oxide.
G = Glycerin (25-30%) as pour depressor.

Results Code: O = no corrosion evident
C = corrosion
S = stain
Sl = slight

Formulation (Acid solution from 21,000 m.w. polymer +)	Results			
	Fe	Zn	Al	Cu
ca. 25% Na ₂ Mo O ₄ (pH-8)	O	S	O	O
20% Na ₂ Mo O ₄ + 4% NaOH (pH-7.5)	O	SlS	O	O
5% NaOH + 6% TEA + G (pH-8)	SlS	C	O	O
34% TEA + G (pH-8)	SlS	C	O	O
10% PO + 30% TEA + G (pH-7.8)	O	C	O	O
10% PO + 33% TEA + G (pH-8.5)	O	C	O	O
10% PO + 33% TEA + G+0.5% Octadecylamine	O	C	O	O
50% TEA + G (pH-8.5)	O	C	C	O
30% TEA + G (pH-8.0)	O	C	O	O
20% TEA + G 10% Tetraethylenepentamine (pH-8.5)	S	C	O	O
12% Tetramethyl guanidine + G (pH-8)	S	SlC	SlC	O
25% TEA + G + 6% Tetramethyl guanidine (pH-8.2)	S	C	O	S
50% TEA + C + 30% Borax (pH-8)	O	C	O	O
14% aq. NH ₄ OH (30% NH ₃) + G	C	C	O	O
12% TEA + 10% aq. NH ₄ OH (30% NH ₃) + G (pH-8)	O	C	O	O
20% TEA + G 14% Tetramethyl guanidine (pH-8.2)	O	C	O	O
15% TEA + G 10% Ethanolamine (pH-8)	O	C	O	O
10% TEA + G 4% NaOH (pH-8)	O	C	O	O
10% TEA + G + ca. 75% Na ₂ WO ₄ (pH-7.2)	S	C	S	S
12% TEA + 30% PO (pH-8.0) *	O	SlC	O	O
12% TEA + 30% PO + 1% Na ₂ WO ₄ *	O	S	O	O
4% TEA + 25% Na ₂ MoO ₄ + 10% NaOH (pH-7)	O	O	O	O
4.0% TEA + 4% Na ₂ MoO ₄ (pH-7)	O	SlC	O	O
2.0% TEA + 7% LiOH + 25% Thiodiethylene glycol	O	SlC	O	O
2.0% TEA + 8% NaOH + 2% Na ₂ CrO ₄ + G	O	O	O	O
2.0% TEA + 8% NaOH + 2% Na ₂ Cr ₂ O ₇ + G	O	O	O	O
2.0% TEA + 8% NaOH + 2% NaWO ₄	O	C	O	O

* Not homogenous. Propylene oxide reaction product, perhaps the hydroxypropyl ester of the thickener, not sufficiently soluble

TABLE VI

FOUR BALL TESTS--ADDITIVES

Base Fluid: Water + ca. 20% Thickener (12,000 m.w. polymer)
 + 20% Potassium Ethane phosphonate.
 + 1.4% Potassium Chromate.

Test Conditions: Room temp., 1800 r.p.m., 15 kg. load, one hour.

<u>Additive</u>	<u>Wear Scar Diameter (mm.)</u>
None	1.12
2% Triethanolammonium dilaurylphosphate	1.20
2% Potassium dialkyldithiophosphate	1.19
1% Chlorendic Acid	1.15
1% Dimercaptothiadiazole	1.14
1% Perfluoroheptamide	1.11
1% Carbowax dioleate (1500)	1.17
1% Peroxyethylene oleylammonium chloride	1.20
1% LP 700 *	1.24
1% LS 500 *	1.15
1% LE 600 *	1.11
5% LE 600 *	1.13
5% LE 500 *	1.09
5% LS 500 *	1.10
1% Butyl Cellusolve	1.22
0.1% Tributylphosphate	1.26
20% Potassium Butane phosphonate **	1.30

* General Analine and Film products.

** Replaced potassium ethane phosphonate in base fluid.

TABLE VII

HELL FOUR BALL TESTS--ADDITIVES

Base Fluid: Water + ca. 20% Thickener (12,100 m.w. polymer)
 + 20% Potassium Ethaneephosphonate.
 + 1.4% Potassium Chromate.

Test Conditions: Room tempt. 1800 r.p.m. 15 kg. load, one-half hour.

<u>Additive</u>	<u>Wear Scar Diameter (mm.)</u>
None	0.97
4% Potassium dialkyldithiophosphate	1.01
5% Powdered Teflon 30	1.04
1% Colloidal Mo S ₂ (Molykote)	0.91
1% Colloidal Mo S ₂ (Dag 206)	1.1
1% Colloidal Graphite (Aquadag)	1.1
1% Ortholeum 162	1.11
1% Dimer Acid (Empol 1018)	0.98
10% Sodium Sulfonate (AA Mahogany Soap)	1.06
1% Diethylthiourea	1.16
5% Laurylpyridinium Chloride	0.90
5% 9,10-Dihydroxysteramide	0.98
5% Tween 20	1.00
5% Tween 80	0.96
5% Renex 30	1.01
5% Renex 68B	0.91
5% Brij 30	0.83
4% Duomeen CD	0.72
2% Brij 30 + 2% Duomeen CD	0.79
1% Duomeen CD	0.99
3% Duomeen T	0.84
3% Vanolube 622	1.04
5% Sucrose	0.86
10% Sucrose	0.58

TABLE VIII

SHELL FOUR BALL TEST--FLUIDS WITH GLYCERIN

Base Fluid: Water + ca. 20% Thickener (12,000 m.w. polymer)
+ 20% Potassium Ethane phosphonate

Test Conditions: Room tempt. 1800 r.p.m., 15 kg. load, one-half
hour.

<u>% Glycerin</u>	<u>Additive</u>	<u>Wear Scar Diameter (mm.)</u>
none	none	0.97
30	none	0.85
30	none	0.89
30	9,10-Dihydroxystearamide	0.62
30	5% Brij 30	0.74
20	2% Duomeen CD	0.81
30	5% Duomeen CD	0.80
30	1% Duomeen CD + 1% Brij 30	0.77
30	1% Duomeen CD	0.75
30	1.5% Potassium Chromate	1.03
30	1.5% Potassium Chromate	0.94

SHELL FOUR BALL TESTS--BIS-HYDROXYMETHYLPHOSPHONIC ACID

Test Conditions: Room tempt., 1800 r.p.m. 15 kg. load, one-half hour.

Additive	Wear Scar Diameter (mm.)
20% Ethane phosphonate--no bis-Hydroxymethylphosphonate	0.97
none--20% bis-Hydroxymethylphosphonate	0.72
none-- 25% bis-Hydroxymethylphosphonate	0.74
none	0.64
1% K_2CrO_4	0.87
1% $K_2Cr_2O_7$	1.10
1% Molybdic Acid	0.62
1% Tungstic Acid	0.75
1% Molybdic Acid + 1% KNO_3 + 0.2% Mercaptobenzothiazole	0.63
1% Salicylic Acid	0.56
1% Boric Acid	0.58
1% Sodium Vanadate	0.90

TABLE X

VICKERS VANE PUMP TESTS--WEIGHT LOSS DATA

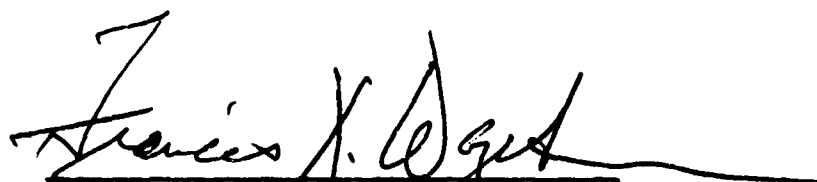
<u>Test No.</u>	<u>Test Duration(hrs.)</u>	<u>Weight Loss (grams)</u>			
		<u>Ring</u>	<u>Vanes</u>	<u>Rotor</u>	<u>End Plates</u>
1	141	13.9	0.039	0.045	0.045
2	140	18.86	0.049	0.137	0.003 (gain)
3	79	7.01	0.034	0.242	1.71
4	86	14.86	0.445	0.008	0.006
5	72	10.44	0.056	0.017	0.036
6	72	3.43	0.009	0.067	0.006 (gain)
7	90	2.21	0.110	0.201	0.004 (gain)
8	74	0.34	0.003	0.030	0.035 (gain)
9	72	1.37	0.009	0.055	0.018 (gain)
10	72	1.15	0.012	0.024	0.007

International Research and Development Corporation

SPONSOR: American Oil Company

COMPOUND: LF-4581 (Water-Based Noninflammable
Hydraulic Fluid).

SUBJECT: Acute Toxicity in Rats and Rabbits


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Collaborators:

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R. G. Geil, D.V.M., Director of Pathology

Date: October 15, 1964

I. SYNOPSIS

Compound LF-4581 was administered orally to albino rats at dosage levels extending from 250 to 10,000 mg./kg. No evidence of toxicity was observed. The LD₅₀ for the test compound was in excess of 10,000 mg./kg.

When applied dermally to the prepared dorsal skin of albino rabbits in the manner described in this report, no evidence of irritation, pharmacotoxicity or mortality was observed.

The results indicate complete innocuousness to the skin of rabbits.

When LF-4581 was instilled into the eyes of albino rabbits in the manner described herein, no evidence of irritation occurred, therefore compound LF-4581 is considered to be non-irritating to the eyes of albino rabbits.

II. COMPOUND

The test compound was received from the American Oil Company, Chicago, Illinois on August 29, 1964. It was a viscous brown fluid in a glass bottle identified as "LF-4581; Water-based Non-flammable Hydraulic Fluid; Contract No. NOBS 90267, L. W. Nixon".

For the purpose of these studies the test compound was considered to be free of impurities.

III. ACUTE ORAL TOXICITY (LD₅₀) IN FEMALE ALBINO RATS

A. METHOD:

Female Charles River albino rats weighing from 215 to 280 grams were used. The test compound was administered orally by

gavage, to 6 rats per dosage level at 250, 500, 1000, 2500, 5000 or 10,000 mg./kg.

Food was withheld from all of the animals for three to four hours prior to administration of the compound. After administration of the compound the animals were housed throughout a 14-day observation period in individual metal cages suspended above the dropping with food and water available ad libitum.

The rats were observed for mortality and pharmacotoxic signs at the following time intervals: 0-60 min., 60-120 min., 120-240 min., 24 hours, and daily thereafter for 13 days.

The test compound was administered undiluted at volumes commensurate with each respective dosage level and the individual body weight of the animals.

B. RESULTS:

1. Pharmacotoxic Signs:

No pharmacotoxic or toxic signs were observed at any dosage level which could be attributable to an effect of the test compound. All animals gained weight normally throughout the experimental period.

2. Mortality:

No animals died at any of the dosage levels tested.

3. Acute Toxicity (LD₅₀):

From the results obtained the LD₅₀ for LF-4581 would be in excess of 10,000 mg./kg. These findings indicate that LF-4581 is a nontoxic substance.

IV. ACUTE DERMAL TOXICITY (LD₅₀) IN THE ALBINO RABBIT

A. METHOD:

Twelve albino rabbits undifferentiated as to sex and weighing from 2123 to 2913 grams were used. The dorsal skin was prepared for the dermal application of the test compound by close clipping of the hair from the back and flanks of each animal with an electric clipper. The skin of one-half of the animals was further prepared by making longitudinal epidermal abrasions through the stratum corneum with a scalpel blade. The rabbits were placed in stocks and LF-4581 was applied once only to the backs of 4 rabbits per dosage level at dosages of 0.5, 1.0 or 2.0 grams/kg., and the body of each rabbit was wrapped with bandage.

After a 24-hour period of exposure to the test compound the the bandages were removed, the back of each animal was wiped dry and the degree of irritation scored. The rabbits also were observed for evidence of mortality and pharmacotoxic effects and returned to their individual cages for observation for a 13-day period.

During the period of observation all of the rabbits were observed once daily for evidence of dermal irritation, death and pharmacotoxic signs. Food and water were available ad libitum throughout the observation period.

Dermal irritation was scored according to the method of Draize on the following page.

CODE

Erythema:

- 0 - None
- 1 - Very slight to slight
- 2 - Well defined or moderate
- 3 - Severe or marked

Eschar not graded only recorded same as necrosis, blanching, and hemorrhagic areas.

Edema:

- 0 - None
- 1 - Very slight to slight
- 2 - Moderate (raised 1.0 to 10 mm.)
- 3 - Marked (raised > 10.00 mm.)

Atonia:

- 1 - Slight (sl. impairment of elasticity)
- 2 - Moderate (slow return to normal)
- 3 - Marked (no elasticity)

Desquamation:

- 1 - Slight (slight scaling)
- 2 - Moderate (scales and flakes)
- 3 - Marked (pronounced flaking with denuded areas)

Coriaceousness:

- 1 - Slight (decrease in pliability)
- 2 - Moderate (leathery texture)
- 3 - Marked (tough and brittle)

Fissuring:

- 1 - Slight (definite cracks in epidermis)
- 2 - Moderate (cracks in dermis)
- 3 - Marked (cracks with bleeding)

B. RESULTS:

The results of this experiment were essentially negative. One rabbit at the 1.0 gm./kg. dosage level exhibited a very mild erythema at 24 and 48 hours after application of LF-4581. All rabbits gained weight normally during the observation period.

Due to the negative results obtained, a table of scores is not included in this report.

According to the results, LF-4581 does not cause skin irritation, nor does its contact with the skin in the manner described cause evidence of adverse systemic effects or mortality.

V. PRIMARY SKIN IRRITATION IN THE RABBIT

A. METHOD:

Six albino rabbits undifferentiated as to sex and weighing from 2203 to 2859 grams were used. The dorsal skin of each animal was prepared for the dermal application of the test compound by clipping an area approximately 3 inches square. The skin of one-half of the animals was further prepared by making longitudinal abrasions with a scalpel blade through the stratum corneum.

The rabbits were placed in stocks and LF-4581 was applied once only to the prepared skin of the animals at a dosage of 0.5 ml./rabbit. The area was then covered with dental dam and gauze and the body of each rabbit was wrapped with elastic bandage.

After a 24-hour period of exposure to the test compound the bandages were removed and the degree of irritation (erythema and edema) recorded. The rabbits were then returned to their individual cages and the skin of each animal again observed and the irritation

scored at 72 hours.

The method of scoring used was according to the following table (Draize):

Erythema:

- 0 - None
- 1 - Very slight to slight
- 2 - Well defined or moderate
- 3 - Severe or marked

Eschar not graded only recorded same as necrosis, blanching, and hemorrhagic areas.

Edema:

- 0 - None
- 1 - Very slight to slight
- 2 - Moderate (raised 1.0 to 10 mm.)
- 3 - Marked (raised >10.0 mm.)

B. RESULTS:

Four-of-six rabbits exhibited a very mild degree of erythema at the 24-hour period of observation. One-of-six still exhibited a very mild erythema at 72 hours. No evidence of moderate to severe erythema was evidenced. Edema did not occur.

The results of this test indicate that LF-4581 is not a primary irritant.

A table of scores has not been included because of the essentially negative results obtained.

VI. EYE IRRITATION TEST IN THE ALBINO RABBIT

A. METHOD:

Six albino rabbits undifferentiated as to sex and weighing from

2.0 to 3.0 kg. were used. Throughout the study period the rabbits were individually housed in metal cages suspended above the droppings. Food and water were available ad libitum.

One-tenth milliliter of LF-4581 was instilled into the conjunctival sac of one eye of each rabbit. The opposite eye served as the untreated control. Prior to instillation of the test compound, and again at termination of the 72-hour observation period, both eyes of each animal were examined with the use of 2.0 per cent sodium fluorescein and a small-window ultraviolet pencil lamp. Other observations for eye irritation were made at 24, 48 and 72 hours. Eye irritation was graded and recorded according to the Scale for Scoring Ocular Lesions on the following page.

B. RESULTS:

The results of this test were essentially negative. No irritation of any nature was observed of the treated eyes of any of the rabbits in this study. Due to the results obtained a table of scores has not been included in this report.

LF-4581 is considered to be non-irritating to the eye when applied in the manner described in this report.

Scale for Scoring Ocular Lesions*

(1) Cornea

(A) Opacity-degree of density (area most dense taken for reading)	
No Opacity	0
Scattered or diffuse area, details of iris clearly visible	1
Easily discernible translucent areas, details of iris slightly obscured .	2
Opalescent areas, no details of iris visible, size of pupil barely discernible	3
Opaque, iris invisible	4
(B) Area of cornea involved	
One quarter (or less) but not zero	1
Greater than one quarter, but less than half	2
Greater than half, but less than three quarters	3
Greater than three quarters, up to whole area	4
Score equals A x B x 5	Total maximum = 80

(2) Iris

(A) Values	
Normal	0
Folds above normal, congestion, swelling, circumcorneal injection (any or all of these or combination of any thereof) iris still reacting to light (sluggish reaction is positive)	1
No reaction to light, hemorrhage, gross destruction (any or all of these)	2
Score equals A x 5	Total maximum = 10

(3) Conjunctivae

(A) Redness (refers to palpebral and bulbar conjunctivae excluding cornea and iris)	
Vessels normal	0
Vessels definitely injected above normal	1
More diffuse, deeper crimson red, individual vessels not easily discernible	2
Diffuse beefy red	3
(B) Chemosis	
No swelling	0
Any swelling above normal (includes nictitating membrane)	1
Obvious swelling with partial eversion of lids	2
Swelling with lids about half closed	3
Swelling with lids about half closed to completely closed	4
(C) Discharge	
No discharge	0
Any amount different from normal (does not include small amounts observed in inner canthus of normal animals)	1
Discharge with moistening of the lids and hairs just adjacent to lids . .	2
Discharge with moistening of the lids and hairs, and considerable area around the eye	3
Score equals (A + B + C) x 2	Total maximum = 20

The maximum total score is the sum of all scores obtained for the cornea, iris, and conjunctivae. Total maximum score possible = 110.

* Lehman, A. J et al., Appraisal of the Safety of Chemicals in Foods, Drugs, and Cosmetics, Assoc. Food and Drug Officials of the U. S., Austin, Texas, 1959.